

4-1960

Transport numbers in pure fused zinc chloride

Arnold Lunden

Chalmers Institute of Technology

Follow this and additional works at: http://lib.dr.iastate.edu/ameslab_isreports



Part of the [Chemical Engineering Commons](#), and the [Chemistry Commons](#)

Recommended Citation

Lunden, Arnold, "Transport numbers in pure fused zinc chloride" (1960). *Ames Laboratory Technical Reports*. 17.
http://lib.dr.iastate.edu/ameslab_isreports/17

This Report is brought to you for free and open access by the Ames Laboratory at Iowa State University Digital Repository. It has been accepted for inclusion in Ames Laboratory Technical Reports by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.

Transport numbers in pure fused zinc chloride

Abstract

Using radioactive tracers, the transport numbers have been measured for both the cation and anion in molten zinc chloride. Due to non-ideal conditions, there was a pronounced tendency for the experiments to give too low values for t^+ and t^- . This tendency became stronger as the current density increased in the cell. An extrapolation to zero current gives $t^+ = 0.6 \pm 0.1$. There was no detectable temperature influence on the transport number in the region from 420°C to close to the boiling point, while measurements in the region below 420°C were uncertain due to the growth of dendrites of deposited zinc metal. No current transport by complex ions could be detected.

Disciplines

Chemical Engineering | Chemistry

IS-114

TRANSPORT NUMBERS IN PURE FUSED
ZINC CHLORIDE

by

Arnold Lundén

**AMES LABORATORY
RESEARCH AND DEVELOPMENT REPORT
U.S.A.E.C.**



IOWA
STATE
UNIVERSITY



Physical Sciences Reading Room

UNCLASSIFIED

IS-114

Chemistry-General (UC-4)
TID 4500, August 1, 1959

UNITED STATES ATOMIC ENERGY COMMISSION

Research and Development Report

TRANSPORT NUMBERS IN PURE FUSED

ZINC CHLORIDE

by

Arnold Lundén

April 1960

Ames Laboratory
at
Iowa State University of Science and Technology
F. H. Spedding, Director
Contract W-7405 eng-82

UNCLASSIFIED

This report is distributed according to the category Chemistry-General (UC-4) as listed in TID-4500, August 1, 1959.

Legal Notice

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty of representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

Printed in USA. Price \$ 1.00 . Available from the

Office of Technical Services
U. S. Department of Commerce
Washington 25, D. C.

CONTENTS

Abstract.	5
EXPERIMENTAL.	16
Materials.	16
Apparatus	17
Procedure	19
RESULTS AND DISCUSSION.	21
ACKNOWLEDGEMENTS.	34

Transport Numbers in Pure Fused Zinc Chloride

By Arnold Lundén⁽¹⁾

Abstract--Using radioactive tracers, the transport numbers have been measured for both the cation and anion in molten zinc chloride. Due to non-ideal conditions, there was a pronounced tendency for the experiments to give too low values for t^+ and t^- . This tendency became stronger as the current density increased in the cell. An extrapolation to zero current gives $t^+ = 0.6 \pm 0.1$. There was no detectable temperature influence on the transport number in the region from 420° to close to the boiling point, while measurements in the region below 420°C were uncertain due to the growth of dendrites of deposited zinc metal. No current transport by complex ions could be detected.

In recent years a number of experiments have been designed for measuring transport numbers in pure molten salts.⁽²⁾ However, the interpretation of the experiments has been questioned, and it has even

(1) On leave from the Department of Physics, Chalmers Institute of Technology, Gothenburg, Sweden.

(2) G. J. Janz, C. Solomons and H. J. Gardner, Chem. Rev. 58, 480 (1958).

been stated, that the whole concept of transference has little significance in pure molten salts. ⁽³⁾ The aim of the present work is to examine critically some factors that might be of influence on the results of the experiments. The general discussion is exemplified by measurements on zinc chloride.

Consider first the general experimental arrangement with two compartments separated by a membrane. Both compartments are at least partly filled with a melt, either a pure salt or a mixture of several components. The membrane can consist of a fritted disc of sufficiently fine porosity, (such as in most "transport number" experiments) a separation column (a packed column of some 20 cm length used in isotope enrichment experiments), ⁽⁴⁾ and an electrophoresis strip, ^(5, 6) or some similar arrangement. Transport of salt through the membrane can be due to a hydrostatic pressure gradient, diffusion and, in the presence of an electric field, electro-osmosis and transference. The distinction between

(3) B. R. Sundheim, J. Phys. Chem. 60, 1381 (1956).

(4) W. Herzog and A. Klemm, Z. Naturforschg 13a, 7 (1958).

(5) M. Chemla, J. Chromatography 1, 2 (1958); C. Mangalo, H. J.

Arnikar and M. Chemla, Compt. rend. 244, 2796 (1957).

(6) H. J. Arnikar, Compt. rend. 244, 2241 (1957).

the two latter entities is obvious if a quasi-lattice model^(7, 8, 9) for the melt is considered,⁽¹⁰⁾ in which case electro-osmosis causes a bulk transport of salt relative to the walls of the capillaries of the membrane, and transference refers to the migration of individual ions in the "lattice". Transference should thus solely be a property of the melt (at the temperature and chemical composition in question), and it should be independent of external conditions such as the type of material used for the construction of the membrane.⁽¹¹⁾ For transference, the transport number, e.g. for a cation, can be defined as $t_t^+ = v^+/w^+$, where v^+ is the velocity of the cation measured relative to the "lattice", while w^+ is measured relative to the anions.⁽¹²⁾ The question arises: Is this theoretically defined transport number t_t identical with, or can it be determined from, the experimentally measured "transport number" t_m ?

(7) A. Lundén, E. U. Monse and N. G. Sjöberg, Z. Naturforschg. 11a, 75 (1956).

(8) A. Klemm, "Physikertagung Wiesbaden" 1955, p. 73.

(9) R. W. Laity, J. Chem. Phys. 30, 682 (1959).

(10) A way to picture the situation is to consider the melt as containing minute crystallites or aggregates held in place by the membrane. For our discussion there is no difference between this view and the quasi-lattice model.

(11) Extreme external pressures might have an influence on the ion mobilities, but this can be neglected for our purposes.

(12) A. Klemm, Proc. Symp. Isotope Separation, Amsterdam, 1957, 275.

Of the four entities contributing to the transport through a membrane, the hydrostatic effect can be measured in an arrangement with a sufficient head of the melt on one side of the membrane. Harrington and Sundheim⁽¹³⁾ have thus measured leakage rates through membranes of five different types, for which the electrical resistance was also measured in order to determine if the membranes could be useful for transference experiments. It might be mentioned in this connection, that there need not be a close correlation between leakage and resistance, e.g. two membranes should be expected to have nearly the same electrical resistance if the total geometrical cross section of their pores is the same, but if one of these membranes has a great many pores of a small diameter while the other one has a few pores with relatively large diameter, the leakages should, according to Poiseuille's law, be considerably higher in the latter case. The hydrostatic flow through a membrane should increase if an electric current passes through the melt, since local heating is likely to give an appreciable decrease in the viscosity of the melt within the pores. The hydrostatic flow of salt through a membrane might well be disturbed by "stickiness"⁽¹⁴⁾ between the melt and parts of the apparatus, which in turn can be due to surface tension effects or to chemical reactions taking place (giving oxides or other reaction products, which might change the properties of the original surfaces).

The diffusion through a membrane can be estimated, if the self-diffusion coefficient is known for the ion in question, since a "cell-constant" can be

(13) G. Harrington and B. S. Sundheim, J. Phys. Chem. 62, 1454 (1958).

(14) M. R. Lorenz and G. J. Janz, J. Phys. Chem. 61, 1683 (1957).

determined by measuring the electrical resistance. It is, however, worth remembering that studies of aqueous solutions⁽¹⁵⁾ and melts on separation columns⁽¹⁶⁾ have shown that the "electrical free space", calculated from measuring the resistance when the column is filled with a liquid of known conductivity, is of the order of 75 per cent of the "geometrical free space", determined by weighing the packing in the column. There might thus be reason to expect that the "cell-constants" are not identical for diffusion and conductivity.

Electro-osmosis and transference are both proportional to the field strength,⁽⁷⁾ which makes it very difficult to distinguish between these two entities when interpreting "transport number" experiments. It is thus possible to introduce a formal transport number for electro-osmosis, t_{os} , by using the following definition:

$$t_{os} = V_{os}/V_{eq} \quad (1).$$

V_{eq} is the equivalent volume of a liquid, and V_{os} is the volume transported by electro-osmosis through a surface perpendicular to the electrical field if the transported charge is 1 Faraday.⁽¹⁷⁾ If we

(15) A. K. Brewer, S. L. Madorsky et al., J. Research Nat. Bur. Standards 38, 137 (1947).

(16) A. Lundén, thesis. Goteborg, 1956, p. 55.

(17) In the assumed formalism, V_{os} is proportional to a zeta-potential and the dielectric constant of the liquid and inversely proportional to the viscosity and conductivity of the liquid, cf, e.g. F. H. MacDougall, "Physical Chemistry", New York, 1943, p. 690.

choose to define V_{os} as positive for transport towards the cathode, the following relations hold:

$$t_m^+ = t_t^+ + t_{os} \quad (2),$$

$$t_m^- = t_t^- - t_{os} \quad (3).$$

Thus $t_m^+ + t_m^- = 1$, independent of the magnitude of t_{os} . However, one of the t_m will be > 1 and the other negative, unless

$$-t_t^+ \leq t_{os} \leq t_t^- \quad (4).$$

So far no experiments with molten salts have given results in contradiction with the limits for t_{os} set in (4).

Sundheim⁽³⁾ has claimed that t_t can be calculated for each experimental set-up from the conservation of momentum within the melt. In this case the experiments actually should give not only t_m but also t_{os} . However, Sundheim has recently modified his theory,⁽¹⁸⁾ so that, due to friction within the melt, momentum can be transferred from the melt to the membrane.

(18) B. S. Sundheim, private communication. This new theory has not been available for study while preparing this paper, and it is thus not possible to consider it in detail. For this reason it is not clear if there are any contradictions between the results of Sundheim's theory and those of a recent theory by Klemm.⁽¹⁹⁾

(19) A. Klemm, Z. Naturforschg. 13a, 1039 (1958).

It might be mentioned for completeness that the contribution from electro-osmosis can change with time if the properties of the surfaces within the membrane change due to chemical reactions between melt and membrane. Such changes might be of importance, e. g. for lithium salts, if the running times are several hours. (7, 20)

It is obvious that t_m is the only measurable entity, e. g. in the indicator-bubble,⁽²¹⁾ electrode displacement^(22, 23) and moving-boundary⁽²⁴⁾ experiments, but the situation is not quite the same for the radioactive-tracer method⁽²⁵⁾ since one might say that the movement of individual ions is followed. Thus, if the two electrode compartments were separated by an ideal membrane with a thickness of the same order of magnitude as the average interatomic distance in the melt, i. e. if an ion only had to make a few "jumps" (perhaps only one jump) in the quasi-lattice structure in order to pass from one compartment to the other, there would be reason to expect that electro-osmosis could be detected even if restriction (4) were fulfilled.

(20) A. Lunden, S. Christofferson and A. Lodding, Trans. Chalmers University of Technology, Goteborg (in press).

(21) F. R. Duke and R. Laity, J. Phys. Chem. 59, 549 (1955).

(22) H. Bloom and N. J. Doull, J. Phys. Chem. 60, 620 (1956).

(23) H. Bloom and D. W. James, J. Phys. Chem. 63, 757 (1959).

(24) F. R. Duke and J. P. Cook, J. Phys. Chem. 62, 1593 (1958).

(25) F. R. Duke and R. A. Fleming, J. Electrochem. Soc. 106, 130 (1959).

However, in all practical arrangements the thickness of the membrane is at least 10^6 times the average interatomic distance, and the measured transport is an average over the displacement of the individual ions, i.e. also in this experiment t_m is the only measurable entity.

So far no experiments with molten salts have given results in contradiction with the limits for t_{os} set in (4). The situation is quite different in molten metals, where studies of the Haeffner-effect (isotope effect in electromigration) have shown that the transport number for the metal ions (equivalent to our t_t^+) is of the order of 10^{-4} . (26) Klemm⁽¹⁹⁾ has recently detected electro-osmosis in mercury, where he estimated that the electro-osmotic mobility was about 17 times higher than that of the transference.

It has usually been assumed for the performed experiments on transport numbers, that the contribution from electro-osmosis is negligible in comparison with the transference, i.e. $t_{os} \sim 0$. This assumption has been supported by the fact that within experimental error, with perhaps one exception, the same transport numbers have been obtained regardless of the membrane material or the method employed. $PbCl_2$ has been studied by the indicator-bubble method with different membranes,⁽²¹⁾ a moving boundary method⁽²⁴⁾ and with radioactive tracers.⁽²⁵⁾ For $NaNO_3$, the transport number determined

(26) A. Klemm, Z. Naturforschg. 9a, 1031 (1954).

by the volume-change method⁽²⁷⁾ agrees with what can be calculated from Arnika's electrophoresis experiments,^(6, 28) but very careful measurements with the indicator-bubble method⁽²⁹⁾ seem to show a slight dependence of t_m on the material used for the membrane. The original electrode-displacement method⁽²²⁾ did not give agreement with the indicator-bubble method,^(21, 14) but after a modification of the former method agreement has been obtained for AgNO_3 ⁽²³⁾. When considering this indirect evidence for $t_{os} \simeq 0$, it might be worthwhile to remember that, at least according to the preliminary experiments,⁽¹⁹⁾ the constitution of the membrane surfaces seemed to have very little influence on the electro-osmosis of molten mercury. Thus experiments performed with different membranes need not rule out the possibility that t_{os} is of importance in molten salts.

In the above discussion we have assumed that the more or less complete dissociation of the salt has given only simple ions. The situation would be different if complex ions with a long life time were formed. For salts such as alkali halides or nitrates, complete dissociation generally is assumed, but for divalent halides it has been questioned^(25, 30)

(27) F. R. Duke and B. Owens, J. Electrochem. Soc. **105**, 548 (1958).

(28) A. Lunden, Z. Naturforschg. **14a**, 801 (1959).

(29) V. A. Lamb and R. J. Labrie, private communication.

(30) F. R. Duke and M. L. Iverson, J. Phys. Chem. **62**, 417 (1958).

whether the primary dissociation dominates or if complete dissociation takes place. In the case of zinc halides there is much evidence for the presence of complex ions^(31, 32) or associations.⁽³³⁾ Consider a divalent halide MX_2 where the following reactions take place in the melt:



Thus, we have the ions M^{2+} , X^- , MX^+ and MX_3^- to which the transport numbers t^+ , t^- , t_c^+ and t_c^- can be ascribed.

Four experiments can be performed with radioactive tracers:

- I. Tagged M in the anolyte can pass through the membrane as M^{2+} or MX^+ , giving $t^+ + t_c^+$ (see below).
- II. Tagged M in the catholyte can pass through the membrane as MX_3^- , giving t_c^- .
- III. Tagged X in the anolyte can pass through the membrane as MX^+ , giving t_c^+ .
- IV. Tagged X in the catholyte can pass through the membrane as X^- or MX_3^- , giving $t^- + t_c^-$.

As an example of the evaluation consider Experiment I, where Z equivalents of charge are passed through the cell. Thus, t^+Z equivalents

(31) W. Bues, Z. anorg. u. allgem. Chem. 279, 104 (1955). M. A. Bredig and E. R. Van Artsdalen, J. Chem. Phys. 24, 478 (1956).

(32) S. N. Flengas and T. R. Ingraham, Can. J. Chem. 35, 1254 (1957).

(33) R. Laity, Annals New York Academy of Sciences (in press).

of M^{2+} ions and $t_c^+ Z$ equivalents of MX^+ ions pass through the membrane towards the cathode, while $t^- Z$ equivalents of X^- ions and $t_c^- Z$ equivalents of MX_3^- ions pass through towards the anode. After the run, the weight of the salt in the anolyte is W_A grams, and in the catholyte, W_C grams. Depending on the method used for measuring the radioactivity, either the total activity, I_A counts/min, or the specific activity, C_A (counts/min)/gr., is determined for the anolyte and for the catholyte I_C and C_C . (The measured activities are corrected for diffusion.) The equivalent weight of the salt MX_2 is M . Because the specific activity is the same in the migrating $(t^+ + t_c^+) Z$ equivalents of salt as in the anolyte, we have

$$\frac{I_C}{(t^+ + t_c^+) Z} = \frac{I_A}{W_A/M}$$

$$t^+ + t_c^+ = \frac{1}{Z} \frac{I}{I_A} C - \frac{W}{M} A = \frac{1}{Z} \frac{C}{C_A} C - \frac{W}{M} C = \frac{1}{Z} \frac{I}{C} C - \frac{1}{M} \quad (8)$$

since $I_C = C_C W_C$ and $I_A = C_A W_A$.

If there is reason to suspect that complex ions are responsible for part of the current transport, it is necessary to perform at least three experiments, II, III and either I or IV, to determine the transport numbers in a melt. Thus, a complete study requires that suitable tracers are available for both cation and anion.

The question arises if t_t can be determined indirectly from types of experiments other than those discussed above, which all give t_m . In

developing a theory for the isotope effect of electromigration in molten salts (and aqueous solutions), Klemm^(8, 12) finds that the transport number t_t is a constant of proportionality in the expression for $\Delta w/w$, the relative difference in velocity for the ions of two isotopes of an element. In Klemm's model there are also a couple of other parameters for which certain assumptions need be made if transport numbers are to be calculated from the rather extensive available data on isotope effects. However, it cannot be expected that such estimations made from the measured isotope effects for zinc and lead halides (ZnCl_2 , ZnBr_2 , PbCl_2 and PbBr_2 , where six out of the total eight isotope effects have been measured so far)⁽⁴⁾ will give more than, at best, very approximate values for t_t . The accuracy would not be good enough to estimate t_{os} from a comparison with t_m .

EXPERIMENTAL

Materials --- Inactive anhydrous zinc chloride was prepared by letting a stream of chlorine gas pass over zinc metal at 500° to 750°C and collecting the distilled zinc chloride in tubes that were sealed off from the apparatus. Four batches of inactive ZnCl_2 were prepared at the same time. Zinc chloride tagged with radioactive zinc (Zn^{65} , half-life 245 days) was made in the same way as the inactive salt.

For the zinc chloride tagged with radioactive chlorine (Cl^{36} , half-life of 4-10 years) another method was needed because the above method would require special arrangements to recover the excess chlorine

after it had passed over the zinc metal. The radioactive chlorine was available as a solution of hydrochloric acid from which silver chloride was precipitated. After drying, the silver chloride was mixed with slightly more than twice the equivalent amount of zinc metal⁽³⁴⁾ and the mixture was slowly heated to about 800°C, whereby zinc chloride was distilled off. Since the product contained considerable amounts of zinc metal, it was purified by redistillation.^(35, 36) However, for most of the runs with radioactive zinc chloride, this was prepared by letting molten anhydrous zinc chloride flow down into a tube containing a small amount of silver chloride of high specific activity. The salt was kept molten long enough to be sure that the mixture of ZnCl_2 and AgCl was homogeneous. The radio active salt thus obtained contained about 0.3 w/o silver chloride.

Apparatus --- Because ZnCl_2 is a very hygroscopic salt, it was considered best to work under a nitrogen atmosphere, and since the salt is fairly volatile at the higher working temperatures the cells were designed as shown in Fig. 1. The cells were made of Pyrex glass or of quartz. The discs were treated as described elsewhere^(25, 37) in

(34) For phase diagram see Landolt-Bernstein, Zahlenwerte und Funktionen. (6th Ed.) Vol. II: 3, p. 13, Berlin, 1956.

(35) For similar methods, see Gmelins "Handbuch der Anorganischen Chemie" (8th Ed.) 32 Erg. band, Weinheim, 1956, p. 847.

(36) This procedure was worked out by Mr. J. P. Cook.

(37) F. R. Duke and A. L. Bowman, J. Electrochem. Soc. 106, 626 (1959).

order to reduce the porosity. In the runs with tagged zinc, the anode consisted of a carbon rod; but when working with tagged chloride, an anode of a droplet of zinc metal was used to prevent liberation of radioactive chlorine gas which otherwise could penetrate over to the compartment with inactive salt. In all runs at temperatures above 420°C , the melting point of Zn, the metal was merely deposited at a tungsten cathode, but when this cathode was used at lower temperatures, the deposited metal grew as dendrites which punctured the disc, thus short-circuiting the cell. For the lowest temperature region, mercury metal was used as a cathode in the hope that the zinc would form an amalgam at the same rate as it was deposited. For the temperature region $356 - 420^{\circ}\text{C}$, molten lead was tried as the cathode, but there was little success because the lead-zinc alloy was not formed fast enough to prevent the growth of zinc dendrites.

The power supply was a rectifier capable of giving up to 500 V DC. The transported electrical charge was measured with a silver coulometer.

The runs at temperatures below 420° were performed in a temperature-stabilized salt bath, while the other runs were made in a vertical oven, which also was temperature stabilized. In the latter runs the cell temperature was measured by means of a Pt, Pt-Rh thermocouple, which was wound around the cell as close to the disc as possible.

Procedure --- For each run one batch of inactive and one of radioactive zinc chloride were selected, cut open, and lowered down into the hot part of the cell, through which nitrogen gas had been flowing during the entire heating-up period. When the salt had melted, the empty holders were pulled out of the cell and the electrodes were inserted; meanwhile, the temperature of the oven was raised to the desired height. The temperature of the cell was measured before the run, at frequent intervals during the run and also some ten minutes after the electrolysis current had been shut off. As expected, the heat generated in the disc was sufficient to raise the temperature of the cell some 3 to 20°C above the temperature in the oven. Due to the fact that the conductivity of ZnCl_2 increases strongly with temperature,⁽³⁸⁾ the current drifted considerably the first seconds after each adjustment of the applied voltage, but in nearly all runs the current was very steady most of the time. The real exception from this was in those runs below 420°C, where dendrites of Zn metal penetrated through the disc. Obviously the dendrites were formed and then dissolved or broken at frequent intervals, thus causing current fluctuations. Simultaneous measurements of the current and the voltage across the cell gave an approximate figure for the resistance. The resistance would vary considerably from cell to cell, evidently because the porosity of the individual discs was not the same.

The electrolysis time was chosen such that the transported charge was of the order of 150 to 200 coulombs in each run. After the run

(38) F. R. Duke and R. A. Fleming, J. Electrochem. Soc. 104, 251 (1957).

the cells were lifted out of the oven to check whether the melt had been at equal heights on both sides of the disc. The cell was quenched and then divided into two samples, catholyte and anolyte, the disc being included with the part to which the radioactivity had been added. The samples were dissolved and then treated in two slightly different ways depending on whether n^{65} or Cl^{36} had been used as tracer.

When working with radioactive zinc the total activity of a sample was measured with a scintillation well counter. For the runs with radioactive chlorine, on the other hand, the specific activity was measured. Here about 0.15 g of silver chloride was precipitated from an ammoniacal solution, weighed, counted with an end-window Geiger Counter and corrected for self-absorption.⁽³²⁾ For all runs the zinc chloride in the samples was determined by an EDTA-titration with naphthyl azoxine⁽³⁹⁾ as indicator.

In all runs with a tungsten cathode the deposited zinc was collected and either weighed or determined by an EDTA-titration. In this way we had a check on the transported electrical charge as determined with a silver coulometer, and there were never any serious discrepancies. As an additional check, the average current was always found to be in agreement with readings during the run.

In a few runs the cell was divided into three samples, where the third sample contained the disc and some salt from each of the two

(39) J. S. Fritz, W. J. Lane and A. S. Bystroff, Anal. Chem. **29**, 821 (1957).

compartments. In these runs both the specific activity and the amount of salt was determined for all three samples, and the original salt contents of anolyte and catholyte were estimated. These runs gave a check that, as expected, the activity in each compartment was distributed homogeneously.

A couple of auxiliary experiments were also performed. Thus, it was found that a considerable exchange of zinc takes place in the molten state between metal and salt. The effect of a hydrostatic head was studied at 512°C by letting a cell stand for 10 hours with a height difference of about 25 mm between the salt in the two compartments. The leakage was found to be 0.4 per cent. Self-diffusion of zinc ions was measured in a run at 674°C .

RESULTS AND DISCUSSION

As seen from the data summarized in Table 1, the runs covered a wide range of temperature and current settings. Of the resistances calculated from the frequent measurements of current and voltage during the runs, either one typical value or the extreme limits are given in Table 1. In a few runs (Nos. 1, 14, 16, 17 and 18) the resistance was very high in the beginning, but after a while there was a sudden change to "normal" conditions. Since this only happened at rather low temperatures where the viscosity of zinc chloride is comparatively high, the plausible explanation is that it took some time before enough salt had penetrated into the disc to establish a good contact between the two compartments. For these runs, Table 1

Table 1. Transport number experiments on molten ZnCl_2

Run No.	Temp. °C	Approx. temp increase °C	Time sec.	Transported charge coul	Mean current ma	Approx. resistance ohms	t ⁺	Remarks
I Runs with Zn^{65} in the anolyte								
1	435	30	10800*	125	11.6 (35)	2100 - 65 k	0.51	
2	440	20	1800	177	98.2	450	0.36	
3	443	4	6000	137	22.9	1600	0.58	
4	457	0	6000	131	21.8	785	0.28	
5	465	60	1200	177	148	380 - 875	0.46	
6	470	10	4000	161	40.1	975	0.52	
7	475	45	1200	153	128	380 - 1740	0.52	
8	506	5	6000	122	20.3	950	0.58	
9	510	15	2400	189	78.6	350	0.36	
10	533	5	6000	131	21.9	1260	0.57	
11	648	12	3000	215	71.7	300	0.49	Quartz cell
12	673	0	6000	147	24.6	100	0.55	Quartz cell
13	434	0	68800	7.7	0.1	400 k - 5M	[0.10]	Disc was fused
14	327	-	10800*	49	4.5 (10)	12 k - 200 k	0.19	Hg cathode
15	343	-	6000	149	25	4.5 k - 33 k	0.12	Hg cathode
16	343	-	10200*	196	19.2 (26)	5 k - 250 k	0.36	Hg cathode
17	332	-	5640*	115	20.3 (31)	1 k - 500 k	0.30 - 1	W cathode; dendrites
18	332	-	7500*	173	23.0	1 k - 200 k	0.23 - 0.63	W cathode; dendrites
19	393	-	10800	182	16.8	910 - 3.3 k	0.11 - 0.37	Pb cathode; dendrites

Table 1. Transport number experiments on molten ZnCl_2 (continued)

Run No.	Temp. °C	Approx. temp increase °C	Time sec	Transported charge coul	Mean current ma	Approx. resistance ohms	t^+	Remarks
II Runs with Zn^{65} in the catholyte								
20	490	9	6000	214	35.7	570	-	$t_c^- < 0.0004$
21	434	-	7500	226	30.1	4 k - 166 k	-	$t_c^- < 0.0004$; Hg cathode
22	660	0	6000	254	42.4	140	-	$t_c^- \approx 0$; see text
III Runs with Cl^{36} in the anolyte								
23	465	10	6000	274	45.6	700	-	$t_c^+ < 0.002$
24	343	-	6000	162	26.9	3500	-	$t_c^+ < 0.0005$
25	426	2	7500	154	20.5	900	0.85	$t^- = 0.15$
26	434	6	6000	140	23.4	950	0.75	$t^- = 0.25$
27	475	10	6000	190	31.7	900	0.66	$t^- = 0.34$
28	475	45	1800	187	103.8	450	0.72	$t^- = 0.28$
29	477	5	6000	129	21.5	700	0.61	$t^- = 0.39$
30	342	-	10800	222	20.6	4500	0.78	$t^- = 0.22$; Hg cathode

*The resistance was very high during the first part of the run, but it dropped suddenly. The mean current was calculated for the whole run and estimated for the latter part of the runs. The latter currents are in parentheses in this table.

gives both the mean current calculated for the whole running time and, in parentheses, an estimated value for the second part of the run.

The current and voltage measurements were also used, as a basis for calculating the wattage, which of course varied very much from run to run (and also, in some cases, during a run), with typical values from 0.4 to 8.3 watts. (The high-temperature runs in quartz cells used 0.1 to 1.5 watts.) We could also make a crude estimation of the total cross-section of the "capillaries" in the disc and of the current density in these capillaries, since

$$A_{\text{eff}} = L/R \quad (9),$$

$$\beta = \frac{L}{f A R} \quad (10),$$

and

$$i = IR / L \quad (11),$$

where

A = geometrical cross-section of membrane,

f = fraction of disc covered by the melt,

L = length of the "capillaries", (40)

A_{eff} = total cross-section of the "capillaries",

100β = free area, percentage,

$\frac{1}{R}$ = specific conductivity of zinc chloride, (32)

I = current, and

i = current density.

(40) It is likely that the pores in the discs consist of a number of cavities connected with each other by small openings. This whole irregular system is for simplicity considered as equivalent to a series of parallel capillaries.

All the discs had a diameter of 1 cm, thus $A = 0.79 \text{ cm}^2$. Since it is difficult to determine the average path length through the membrane, we found it sufficient merely to use the thickness of the discs, approximately 1.5 mm, as L in our calculations. For this reason the calculated free areas might be somewhat lower and the current densities somewhat higher than the "true" values. Since the conductivity of zinc chloride is extremely temperature dependent,⁽³⁸⁾ the calculations are very sensitive to errors in estimating the temperature in the capillaries.⁽⁴¹⁾ For this

(41) It is obvious that the temperature distribution is very inhomogeneous in the discs, since the heat production is concentrated to the salt-filled "capillaries". The heat is then transported through the disc to the other parts of the cell. The heat conductivity of molten ZnCl_2 is not known, but it is possible to make some very crude estimations of existing temperature gradients by assuming that the heat production is homogeneous throughout the disc, and that heat conduction in the axial direction dominates. The heat conductivity of Pyrex glass can be estimated to be approximately $0.015 \text{ W cm}^{-1} \text{ degree}^{-1}$, cf. e.g. G. W. Morey, "The Properties of Glass", 2nd Ed. New York, 1954, p. 220. The difference in temperature between the center of the disc and the ends would then be 1.6°C for 1 watt and 13°C for 8.3 watts dissipated in the disc. Due to the concentration of the heat production to the capillaries, the actual temperature differences are likely to be higher. Because of the lack of information on the actual temperatures in the discs, the conductivity at the measured cell temperature was used when calculating β and i .

reason the uncertainty in the β and i obtained was considered greatest for the runs at low temperatures or with high currents. Although in one run an extreme value of 1.6 per cent was found for β , the runs with currents less than 30 ma gave values between 0.2 and 0.5 per cent. Further considerations showed that the most likely free area of a disc was 0.3 to 0.4 per cent. The limits for the current densities in our runs with Pyrex cells were found to be 5 and 25 amps/cm². For one of the runs with a quartz cell the current density was found to have been 47 amps/cm². It might be mentioned, that for a disc with a free area of 0.35 per cent, a current density of 10 amps/cm² would mean a total current of 27.5 ma. For previous work with similarly prepared membranes^(25, 37) no measurements of the current density have been reported, but if the present estimation of the free area is of the right order of magnitude, this previous work might have been done with current densities of the order of 100 amps/cm².

The transport numbers were calculated according to Eq. (8) and corresponding equations. For the runs with Zn⁶⁵ in the anolyte (Type I), the activity I_C measured for the catholyte was corrected for the activity in the deposited zinc. Because the zinc that is being deposited always has the same specific activity as the salt, the final specific activity of the deposited metal would be half that of the salt at the end of the run if no exchange of zinc took place between salt and metal, while a complete exchange would give the same specific activity. From our exchange experiment (see above) we concluded that the specific activity of the

deposited metal could be considered as approximately $0.75 C_C$. (The amount of deposited metal was too small to allow a direct measurement of the activity.) The correction was usually of the order of 1 per cent of I_C .

The above-mentioned diffusion experiment at 674°C confirmed that a sufficient accuracy was obtained in our estimations, if the self-diffusion coefficient for zinc in ZnCl_2 was assumed to be of the same order of magnitude as the coefficient measured for zinc in ZnBr_2 .⁽⁴²⁾ The self-diffusion coefficient is not known for any anion in a zinc halide. The contribution from self-diffusion was of importance when calculating the transport numbers at higher temperatures. For the run at 673°C , 5 to 10 per cent of the activity was transported by diffusion.

Of the runs for measuring t_C^- and t_C^+ (Type II and III), the four runs in Pyrex cells showed such a small transport of activity through the membrane, that it was difficult to distinguish from the background. Estimations gave the result that self-diffusion alone was more than sufficient to account for the whole transport, and the measured t_C^- (runs 20 and 21) and t_C^+ (runs 23 and 24) are to be considered as upper limits, likely to be at least an order of magnitude too high. The run at 660°C (No. 22) gave an uncorrected value for t_C^- of 0.036, of which, however, about $2/3$ should be due to self-diffusion according to the above-mentioned test. The remaining transport was due to a hydrostatic head of about 3 mm. Thus, also in this run t_C^- is very small, and we can conclude that no transport by complex ions has been

(42) L. E. Wallin and A. Lunden, Z. Naturforschg. 14a, 262 (1959).

detected in any part of the investigated temperature range, and that t_c^+ and t_c^- can be neglected in comparison with t^+ and t^- when interpreting the runs of Type I and IV.

Regarding the measured t^+ and t^- , it is obvious that the spread in the obtained results is considerably higher than what can be expected from the statistical error of the measurements. Thus, the accuracy should be better than 2 per cent for the chemical analysis and 1 per cent for the transported charge. Concerning the activity measurements, I_C/I_A was usually measured with a probable error of less than 1 per cent when working with Zn^{65} . The error in the corresponding ratio, C_A/C_C , for the runs with Cl^{36} was higher because some of the measured samples had a total activity of the order of only 50 per cent above background. Adding up the contributions from the individual measurements, the result for most runs has a probable error of about ± 0.02 , while the extreme values for t^+ (Runs 3 and 8, resp. 4) differ by a factor of 2. The question arises: How can the spread be explained by the variation in parameters from run to run? In experiments with non-hygroscopic salts it is possible to avoid hydrostatic heads by weighing up the salt before adding it to the cell, but in the present experiment this could not be done. However, for more than half of the t^+ and t^- -runs, our check afterwards showed that the hydrostatic head was less than 1 mm, and for the remaining runs there was no correlation between t^+ (or t^-) and the occurrence of a head of a couple mm on either side of the disc. Neither would this be expected from a comparison with the above mentioned check run at 512°C. It was not considered worthwhile to perform any calculations

on the expected hydrostatic flow at different temperatures, since the viscosity of ZnCl_2 has only been measured in the region $320 - 380^\circ\text{C}$, where it has been found to decrease by nearly one order of magnitude.⁽⁴³⁾ As can be seen from the table, there is no evident correlation between t^+ and the temperature, at least not in the region above 420°C . Below this temperature the measurements are very uncertain, since in at least 3 of the runs (Nos. 17, 18, 19) dendrites of zinc had grown into the disc. For these runs, where either a tungsten or a lead cathode was used, it was possible to weigh the zinc that was deposited in the cathode compartment, which might be considered as a lower limit for the transported charge, while the upper limit was of course measured with the coulometer. (In the run with a lead cathode, part of the deposited zinc might have formed an alloy with the lead instead of being recovered as pure zinc after the run.) In the four runs (Nos. 14, 15, 16 and 30) with a mercury cathode, there were no indications of dendrites. Neither rapid fluctuations in the current, nor any deposited metal was to be found in the disc. However, two of the runs (Nos. 14 and 15) still gave t^+ - values below the "lower limit" set by the runs (Nos. 17 and 18) with a tungsten cathode. The interpretation of all the runs below 420°C is thus uncertain, although a change in transport number might have been expected in at least the lower part of this region, since the general systematics for divalent halides⁽⁴⁴⁾ predicts that $t^+ = 0$ in solid ZnCl_2 .

(43) J. D. MacKenzie, private communication.

(44) Ref. 29, Vol. III: 6, p. 243, Berlin, 1959.

The remaining parameter to be considered is the current, and, as can be seen in Table I, there are strong indications that t^+ is influenced by the current. Thus the four highest values for t^+ (runs 3, 8, 10 and 12) were all obtained for currents below 25 ma, and in this current range there is only one run (No. 4) that differs from the others more than by the experimental error ± 0.02 .⁽⁴⁵⁾ For the higher currents, there is much more of a spread in the obtained t^+ . When it comes to the work with Cl^{36} , the highest value for t^- occurs for a run (No. 29) with a current less than 25 ma, but the other two runs in this current range give low t^- -values. It might be considered more proper to assume that either the current density or the dissipated heat is the fundamental parameter rather than the current, but a plot of t^+ against either of these entities gives essentially the same result as when plotted against current. A conclusion that the transport number depends on the current would be easy to accept if it could be explained as a mere temperature effect, meaning that the measured transport number does not correspond to the temperature of the cell but to the higher temperature produced by local heating in the capillaries of the membrane. As no direct correlation between t^+ and the temperature has been found (see above), there remains the conclusion that the current, as such, has an influence on the transport number. This is very unsatisfactory, since it is more or less in conflict with the basic models underlying the whole concept of transport numbers. Nor has any influence of the current on the transport number been reported from previous experiments with other salts. Thus, Bloom and James⁽²³⁾ varied the current by a factor of four when measuring t^- in AgNO_3 .

(45) Because of the considerable contribution from self-diffusion, Run 12 has an experimental error of ± 0.06 .

The "current effect" might be easier to understand after considering the most striking result of the runs, namely that the t_m^+ -values obtained as $1 - t_m^-$ from the runs with Cl^{36} do not agree with the t_m^+ -values of the runs with Zn^{65} . The division in two groups on either side of $t^+ = 0.60$ is significant, since, in spite of the great spread within both groups, not a single result falls among the data obtained with the other method. The trivial explanation that a systematic error has occurred either in the determination of the transported charge or the amount of salt, Z and W of Eq. (8), can be ruled out since the methods used for determining these two entities have not only been tested carefully but also cross-checked against each other by EDTA-titrations on the deposited zinc. A possible source of error would be if the radioactive ions that passed through the membrane did not spread uniformly in the compartment but instead were concentrated very close to the membrane, which means that they would stay with the membrane in the active sample, (see above). This possibility was ruled out by dividing the cells of some runs into three samples with the salt that was next to the disc on both sides, forming a third sample. These runs did not differ in their results from the other runs.

It is thus evident that the chosen experimental arrangement gives the rather unexpected result that $t_m^+ + t_m^- < 1$. Such a result can only be obtained by using the radioactive tracer method, while for all the other methods used for transport number measurements, there is no way to distinguish between an arrangement for measuring t^+ and one for t^- , i.e. $t_m^+ + t_m^- = 1$ per definition. Thus, it would have been interesting to

supplement the present investigation by making some runs with the indicator-bubble method. However, the unusually high viscosity of $\text{ZnCl}_2^{(43)}$ makes it likely that "stickiness" will cause spurious results in all methods proposed, except the tracer method. In all previous work with this method only t_m^- has been measured and it has thus been assumed that $t_m^+ = 1 - t_m^-$. Even if this assumption has been found not to hold in the only experiment where it has been tested, there is no reason to expect in general that the radioactive tracer method should give results deviating from other methods. It was found that, as mentioned above, the same result was obtained with all the methods used for measurements on PbCl_2 . The question arises whether the unexpected discrepancy found in the present experiment between t^+ and $1 - t^-$ might be due to the properties of the chosen salt, ZnCl_2 . The experimental result might at first sight be interpreted by saying that both ionic and electronic conduction occurs in molten ZnCl_2 , but by weighing the deposited Zn we have shown that Faraday's law was obeyed⁽⁴⁶⁾ in ZnCl_2 as well as in the cases of other molten salts.

The explanation can be sought in the fact that the current density is of the order of 300 times higher in the membrane than in the bulk of salt. The temperature in the "capillaries" is considerably higher than in the bulk of salt, and, since the activation energies are unusually high for

(46) This could not be checked for the runs below 420°C , where there was interference due either to dendrite growth or to the deposited zinc forming an alloy with mercury.

ZnCl_2 , the conductivity, self-diffusion, viscosity, degree of association⁽³³⁾ and other properties differ markedly between the salt in the membrane and the bulk of the salt. The salt in the cell might thus be divided into three zones, where the salt in the central zone, i. e. in the "capillaries" of the membrane, is separated from the two adjoining zones by sharp boundaries at which all physical properties change significantly. It is likely that the migration of ions across these two boundaries is suppressed in comparison with the migration within the three homogeneous zones, and this would mean that the mechanism for charge transport becomes complicated. The simple transport by ions passing through the boundaries from one zone to the other has to compete with a charge exchange between ions on either side of the boundary, perhaps by simultaneous charging and discharging of two ions in the "quasi-lattice". If transport mechanisms of the kind indicated here exist at the boundaries, it is to be expected that the deviation from ideal conditions increases with increasing current density, or properly increasing wattage, and this seems to be the case at least for the measured t^+ , while the number of t^- -runs is too small to allow definite statements. If an extrapolation to zero current is made for t^+ -runs (No. 3, 5, 7, 8 and 10) the limiting value will be close to $t_m^+ = 0.6$, and about the same limit will be obtained for the three t^- -runs that gave the highest t^- -values. Thus, for ideal conditions a transport number of $t^+ = 0.6 \pm 0.1$ can be expected.

One run (No. 13) was actually performed with a very low current, but this was because the disc was fused at least on one side, and the current density certainly was high in the minute "capillaries" that might have

existed. This run gave a very low value for t^+ , which might indicate that most of the charge transport was due to the conductivity of the glass, while the fraction of the current conducted by the glass is negligible in the other runs.

At 500°C the equivalent volume of ZnCl_2 is 28.0 cm^3 ,⁽⁴⁷⁾ which means that at a current density of 10 amps/cm^2 the velocity of a cation relative to the anions would be $3 \cdot 10^{-3} \text{ cm/sec}$. The time for an ion to traverse a distance of 1.5 mm (the thickness of the disc) is thus 50 sec . This is thus the order of magnitude for the average time for an ion to migrate through the membrane. The average distance between two zinc ions in the melt is $4.6 \cdot 10^{-8} \text{ cm}$, and if the mechanism is simplified by assuming that the zinc ions form a simple cubic lattice in which an ion moves by jumping from one lattice position to an adjacent vacancy, the average time an ion remains in a certain position would be of the order of $1.5 \cdot 10^{-5} \text{ sec}$ for the specified current density of 10 amps/cm^2 . These crude estimations can be used when discussing what information the experiment has given regarding complex ions. The upper limit of about 0.00004 obtained for both t_c^+ and t_c^- proves that an assumed transporting complex ion must dissociate before the ion has traversed more than a small fraction of the distance through the membrane. Thus the maximal lifetime of such an ion is of the order of 1 sec . The concept of complex ions is meaningful when interpreting absorption spectra of fused salts.^(48, 49) The time for one vibration

(47) W. Klemm, Z. anorg. u. allgem. Chem. **152**, 247 (1926).

(48) D. M. Gruen, J. Inorg. Nuclear Chem. **4**, 74 (1957).

(49) B. R. Sundheim and J. Greenberg, J. Chem. Phys. **28**, 439 (1958).

to occur is several orders of magnitude less than the average time between two jumps in our above mentioned crude model. Thus, transference experiments and spectroscopic work might well give results that appear to be in conflict with each other regarding the existence of "complex ions".

The present experiment and data on conductivity, self-diffusion, etc. are in fair agreement with the following qualitative model for conduction in ZnCl_2 . Most of the ions are associated and more or less tightly bound in a "quasi-lattice structure", in which a few Zn^{++} and Cl^- ions are free to move. The fraction of mobile ions is a function of the temperature, and an individual ion can alternatively be mobile or associated in the quasi-lattice.

ACKNOWLEDGEMENTS

I am much indebted to Prof. F. R. Duke and Mr. J. P. Cook for stimulating discussions during the experiments and to the former also for valuable criticism of the manuscript.